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Exchange and Aquation Studies with Thiocyanato Complexes<sup>1</sup>

by

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ABSTRACT

The first order aquation rate constants for the replacement of thiocyanate by water have been determined for the complex ions  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$ ,  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$ , and trans  $\text{Co en}_2(\text{SCN})_2^+$ . For the first two, the respective values in  $\text{min}^{-1}$  are  $k = 1.17 \times 10^{13} \exp.(-24,900/RT)$  and  $k = 0.85 \times 10^{13} \exp.(-26,800/RT)$ , with  $\Delta S^\ddagger = -7.8, -8.4$  E.U. The rate of bimolecular exchange of thiocyanate ion with the  $\text{SC}^{14}\text{N}$  labelled complexes was found to be not more than a few percent of the aquation rates, being undetectable against the aquation background.

The aquation of  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$  was found to be catalyzed by thiocyanate ion while for  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$  no such enhancement of rate was found. An interpretation of this and other aspects of ligand replacement with trivalent chromium and cobalt complexes is presented whereby it is inferred that an  $\text{S}_{\text{N}}2$  mechanism holds for chromium complexes and an  $\text{S}_{\text{N}}1$  mechanism for those of cobalt.

During recent years renewed interest has developed in the nature of the mechanism whereby one ligand replaces another in covalently bonded complex ions. Evidence has been sought in exchange studies and in the kinetics of net reactions. Thus the rapid exchange observed with tetracoordinated complex ions, such as of radiocyanide ion with  $\text{Ni}(\text{CN})_4^{-2}$ <sup>3,4</sup> and  $\text{Pd}(\text{CN})_4^{-2}$ <sup>3</sup>, and of radiocyanide and

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- 3 A. W. Adamson, J. P. Walker and M. Volpe, THIS JOURNAL, 72, 4030 (1950)  
 4 F. A. Long, ibid., 73, 537 (1951)
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halide ions with  $\text{HgX}_4^{-2}$  complexes<sup>3,5</sup> has been thought to result from a ready

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- 5 A. A. Grinberg and L. E. Nikolskaya, Zhur. Priklad. Khim. 24, 893 (1951)
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bimolecular reaction involving a five coordinated transition state employing the available outer p orbital<sup>6,7</sup>. For the hexacoordinated complexes of trivalent

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- 6 A. W. Adamson, J. P. Walker, and W. B. Wright, THIS JOURNAL, 73, 4786 (1951)  
 7 H. Taube, Chem. Rev., 50, 69 (1952)
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ions, one sequence appears to be  $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$  in order of decreasing lability, as in the exchange of radiocyanide ion with the hexacyano complexes<sup>3</sup>. It was pointed out that this sequence paralleled the expected ease of accommodation of a seventh pair of electrons in forming the heptacoordinated transition state for a bimolecular reaction<sup>6</sup>. A general interpretation of substitution reactions along such lines is presented in an excellent review by H. Taube<sup>7</sup>.

The alternative to the bimolecular or  $\text{S}_{\text{N}}2$  mechanism would be a dissociation or  $\text{S}_{\text{N}}1$  type process leading to an intermediate of  $(n-1)$  coordination number. Such a mechanism would be a plausible possibility for  $\text{Co(III)}$  complexes since to add a seventh group, an outer orbital would be required; the instability for such a case is well demonstrated by the failure of  $\text{Co(II)}$  to complex more

than five cyanides<sup>8</sup>. Apart from the complications due to specific ion inter-

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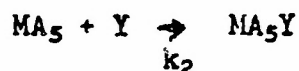
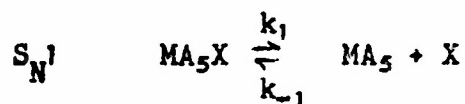
<sup>8</sup> A. W. Adamson, THIS JOURNAL, 73, 5710 (1951)

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action effects, to be considered later, the two mechanisms would be exemplified as follows:



$$R = k_1 (MA_5X) (Y)$$



$$R \text{ (stationary state)} = k_1 (MA_5X) \frac{1}{1 + k_{-1}/k_2 Y} \quad (1)$$

Although the kinetics of ligand replacement have been determined for several aqueous systems, no clear cut distinction between the above alternatives has proven possible. In the case of net reactions, quantitative kinetic studies are available only for aquation<sup>9</sup> and hydrolysis<sup>9a,b</sup>. For  $Y = H_2O$ , the observed

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- <sup>9</sup> (a) J. N. Bronsted and R. Livingston, *ibid.*, 49, 435 (1927); (b) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, 17, 1167 (1949); (c) F. J. Garrick, *Trans. Far. Soc.*, 33, 486 (1947), 34, 1088 (1938); (d) F. Basolo, J. G. Bergman and R. G. Pearson, *J. Phys. Chem.*, 56, 22 (1952); (e) H. Taube and F. A. Posey, THIS JOURNAL, 75, 1463 (1953), and others.
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first order kinetics may simply reflect the inability to vary solvent concentration, although Taube and Posey<sup>9e</sup> infer a greater plausibility for the  $S_N1$  mechanism in the case of  $Co(NH_3)_5(SCN)^+$  and Basolo *et al*<sup>9d</sup> likewise, from steric effects, in the case of complexes of the type  $Co(AA)_2Cl_2^+$ . Although the reverse of aquation ( $X = H_2O$ ) is bimolecular, the mechanism could still be  $S_N1$ , with  $k_2$  small. On the other hand, the second order kinetics and increased reaction velocity with  $Y = OH^-$ , as with  $Co(NH_3)_5Br^{++}$ <sup>9a,b</sup> suggest an  $S_N2$

process. In a recent series of publications, Brown, Ingold and Nyholm<sup>10</sup>

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- 10 D. D. Brown, C. K. Ingold, and R. S. Nyholm, J. Chem. Soc., 2675 (1953); D. D. Brown and C. K. Ingold, ibid., 2680 (1953); D. D. Brown and R. S. Nyholm, ibid., 2696 (1953)
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found similar second order kinetics for substitution of  $\text{N}_3^-$ ,  $\text{NO}_2^-$  and  $\text{CH}_3\text{O}^-$  ions for  $\text{Cl}^-$  in cis  $\text{Co en}_2\text{Cl}_2^+$  in methanol solution and concluded that the  $\text{S}_{\text{N}}2$  mechanism prevailed. An alternative interpretation is given under Discussion, below.

Returning to aqueous systems, the few quantitative studies of exchange kinetics have not been decisive. Thus the rate of exchange of radiocyanide ion with  $\text{Fe}(\text{CN})_6^{+3}$  and  $\text{Mn}(\text{CN})_6^{-3}$  was found to be independent of cyanide concentration<sup>3,6</sup>, but under conditions suggesting that the probable mechanism involved an aquation equilibrium. Harris and Stranks<sup>11</sup> proposed a bimolecular

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- 11 G. M. Harris and D. R. Stranks, Trans. Far. Soc., 48, 137 (1950)
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exchange of radiobicarbonate with a  $\text{Co}(\text{NH}_3)_4(\text{HCO}_3)(\text{H}_2\text{O})^{++}$  intermediate to explain their data on the exchange of radiocarbonate ion with  $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ . Their data do not lead unambiguously to this conclusion, however; in addition, the ability of the carbonatogroup to shift from a bidentate to a monodentate character complicates the question of the coordination number of the transition state.

Taube et al<sup>12</sup> have studied the measurably fast exchange of water with

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- 12 J. P. Hunt and H. Taube, J. Chem. Phys., 18, 757 (1950), R. Plane and H. Taube, J. Phys. Chem., 56, 33 (1952)
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$\text{Cr}(\text{H}_2\text{O})_6^{+3}$ , and Rutenberg and Taube<sup>13</sup> that with  $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{+3}$ . As with the

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13 A. Rutenberg and H. Taube, ibid., 20, 823 (1952)

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net aquation kinetics no definitive answer is possible, but inferences may be drawn from the specific ion effects observed.

The present work was initiated in an attempt to make a more telling test for some second order character in the kinetics of ligand replacement with hexacoordinated complexes. The particular choice was to study the exchange of thiocyanate ion with the complexes  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$ ,  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$ , and trans  $\text{Co en}_2(\text{SCN})_2^+$ . An exchange of the anion of a strong acid with a positively charged complex ion was chosen on the grounds that the rates should then be pH independent on the acid side, and that the opposing charges might favor a bimolecular process. The thiocyanate system was selected because of the greater stability towards aquation (as compared to the corresponding halogen complexes). Finally, any background of aquation should be simpler to treat with a mixed acido-amine type of complex for which aquation would be limited to one or two steps, as opposed to the situation with the hexacyanide complexes for which aquation, once initiated, generally proceeded to a complete hydrolysis.

### Experimental

Preparation of Materials. (a) Trans  $[\text{Co en}_2(\text{SCN})_2]\text{SCN}$  and Trans  $[\text{Co en}_2(\text{SCN})_2]\text{ClO}_4$ . Trans  $[\text{Co en}_2(\text{SCN})_2]\text{SCN}$  was prepared from the corresponding dichloro compound by treatment of the latter with concentrated thiocyanate solution in boiling water, as described by Werner and Braunlich<sup>14</sup>. The active

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14 A. Werner and F. Braunlich, Z. anorg. Chem., 22, 91 (1900)

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complex was prepared by admixing some  $\text{KSCN}^{14}$  of high specific activity with the inactive thiocyanate. The water of crystallization was removed by heating at two hours at  $120^\circ\text{C}$  and the anhydrous salt was employed throughout. Treatment of the thiocyanate salt of the complex in aqueous solution with sodium perchlorate yielded the slightly soluble perchlorate salt. Anal. Calcd. for  $(\text{Coen}_2(\text{SCN})_2)_3\text{ClO}_4$ : Co, 14.9% Found: 15.0%; ionic thiocyanate, trace. Calcd. for  $[\text{Co en}_2(\text{SCN})_2]\text{SCN}$ : Co, 16.9%, ionic SCN, 16.1%. Found: Co, 16.7%, ionic SCN, 16.4%.

(c)  $[\text{Co}(\text{NH}_3)_5(\text{SCN})](\text{SCN})_2$  and  $[\text{Co}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4)_2$ .  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$  was prepared according to Inorganic Syntheses<sup>15</sup>. By treatment with a slight

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15 Fernelius, "Inorganic Syntheses", Vol. I, McGraw Hill Book Co., Inc., New York, New York, 1939, p. 186.

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excess of freshly precipitated silver carbonate in aqueous suspension, conversion into  $[\text{Co}(\text{NH}_3)_5(\text{OH})]\text{CO}_3$  was effected, and then to  $[\text{Co}(\text{NH}_3)_5(\text{SCN})]\text{SO}_4$  by the method of Werner and Muller<sup>16</sup>. The sulfate salt was converted to the per-

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16 A. Werner and H. Muller, Z. anorg. Chem., 22, 101 (1900)

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chlorate by precipitation with sodium perchlorate, and to the thiocyanate salt by saturating the solution with sodium thiocyanate. Anal. Calcd. for

$[\text{Co}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4)_2$ : Co, 14.7%. Found: 14.8%. Calcd. for  $[\text{Co}(\text{NH}_3)_5(\text{SCN})](\text{SCN})_2$ : ionic SCN, 36.4%. Found: 36.7%.

(c)  $[\text{Cr}(\text{NH}_3)_5(\text{SCN})](\text{SCN})_2$  and  $[\text{Cr}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4)_2$ .  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was prepared according to the method of Werner and Halban<sup>17</sup>, and was converted

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17 A. Werner and J. V. Halban, Ber., 2668 (1906)

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to  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$  by heating a solution ca. 2M in sodium thiocyanate and acidified with acetic acid for a (very) few minutes at 90°C. The mixture was quenched when the color change from rose to orange was complete for a test sample of precipitate obtained periodically by filtering off a small portion of the reaction mixture. Either the thiocyanate or the perchlorate salt was obtained, depending upon whether or not sodium perchlorate had also been added to the reaction mixture. In view of the large excess of free thiocyanate required for this reaction, the labelled complex was prepared by boiling for a few minutes a concentrated solution of  $[\text{Cr}(\text{NH}_3)_5(\text{SCN})](\text{SCN})_2$  with a small amount of sodium radiothiocyanate and then precipitating the perchlorate salt. Anal. Calcd. for  $[\text{Cr}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4)_2$ : total SCN, 14.3%. Found: 14.7%, and a trace of ionic SCN.

(d) Conversion of the perchlorate salts of the complexes to the thiocyanate salts. Although the thiocyanate salts of  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$  and  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$  could be prepared directly, it was difficult to do so by the normal methods if it was desired that only the inner thiocyanate be labelled. Such complexes were prepared from the corresponding active perchlorate salts either by passing a solution through the thiocyanate form of an anion exchanger, or by adsorbing the salt on a cation exchanger and eluting with concentrated sodium thiocyanate solution. Since by the former method, the resulting solution was quite dilute because of the slight solubility of the original perchlorate salt, excess sodium thiocyanate was added, and an extraction into cyclohexanone

carried out. The solid complex was recovered by precipitation from the cyclohexanone solution by the addition of ether and toluene, then washed and dried.

(e) Sodium radiothiocyanate. Potassium radiocyanide was obtained as such from Tracerlab, Inc., and converted to radiothiocyanate by refluxing with powdered sulfur in acetone containing a few drops of water (50 mg KCN, 50 mg S, 8 ml. acetone). After an hour, the solution was evaporated to dryness, acetone added, and the product filtered to remove unreacted potassium cyanide. The filtrate was again evaporated to dryness, and the residue boiled a few minutes with animal charcoal suspended in a small amount of water, and then filtered. The potassium radiothiocyanate obtained upon evaporating the filtrate to dryness was either used as such, or converted to sodium radiothiocyanate by passage through the sodium form of a cation exchanger.

Analytical Procedures. (a) Cobalt. The cobalt complexes containing ethylenediamine were decomposed by boiling (gently) with a mixture of perchloric and nitric acids for three hours, then for an hour with added sulfuric acid. The resulting cobaltous sulfate solution was diluted and determined by the method of Laitenen and Burdett<sup>18</sup>. The pentamine complexes were decomposed by

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<sup>18</sup> H. A. Laitenen and L. W. Burdett, Anal. Chem., **23**, 1268 (1951)

fuming to dryness with sulfuric acid, diluting and adjusting the pH to near neutrality. The cobalt was then determined by the method of Cartledge and Nichols<sup>19</sup>.

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<sup>19</sup> G. H. Cartledge and P. M. Nichols, ibid., **13**, 20 (1941)

(b) Ionic Thiocyanate. The ionic or unbound thiocyanate present in a solution was determined by adding a measured volume to a much larger one of a standard reagent 0.5 f in ferric nitrate and 0.5 f in perchloric acid, giving a



thiocyanate formality of ca.  $10^{-4}$ . The optical density of the resulting ferric thiocyanate complex was determined at 460 m $\mu$  with a model DU Beckman spectrophotometer and compared with that of a standard.

(c) Total Thiocyanate. Coordinately bound plus ionic thiocyanate was determined for the chromium complexes by destroying the compound in hot concentrated alkali. The resulting deep green solution was acidified with perchloric acid, chromic hydroxide precipitated out with alkali, and after centrifugation, the supernatant was acidified and the thiocyanate ion concentration determined as in (b). It was found necessary to dissolve and reprecipitate the first precipitate twice, analyzing each supernatant for the additional small portions of free thiocyanate that were present.

It was not possible to determine bound thiocyanate for the cobalt complexes; destruction of the complex was accompanied by oxidation of much of the bound thiocyanate.

Counting and Sample Preparation Procedures. The  $C^{14}$  radioactive samples were counted by means of a flow counter and conventional scaling circuit. An adoption of the method employed by Haissinsky and Pullman<sup>20</sup> of counting "in-

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20 M. Haissinsky and B. Pullman, J. de Phys. Rad., Ser. VII, 8, No. 2, 33 (1947)

finitely thick" samples, was used. About 60 mg of material to be counted, a washed and dried precipitate of reproducible composition, was gently spread in a cylindrical depression 1.4 cm in diameter and 0.2 cm deep which was machined out of a thick aluminum disk. A steel cylinder of diameter slightly less than that of the depression was then carefully pressed against the sample, and by sharply hitting the cylinder with a mallet, the sample was compressed to a compact mat. Any surplus solid on the rim of the disk was carefully wiped off. This technique was found to be as accurate and more rapid than the thin sample

one employed in earlier work<sup>3</sup>. Since the samples are thicker than the range of the beta particles from  $C^{14}$  the measured activity is proportional to the specific activity of the material.

Ionic thiocyanate was counted as cuprous thiocyanate obtained by adding a small amount of cuprous chloride in 6N hydrochloric acid to an acidified solution containing the radiothiocyanate, then washing the precipitate with water, alcohol and ether, and drying it at 100°C. Where the starting solution contained radio active complex it was necessary to remove it very completely to avoid coprecipitation with the cuprous thiocyanate. This was accomplished by first precipitating the perchlorate salt of the complex, then extracting the remainder by three successive extractions with cyclohexanone. The resulting water white solution was freed of cyclohexanone (which tended to react with the cuprous salt) by two ether extractions, the ether removed by boiling the water layer gently, and then, finally, the cuprous thiocyanate was precipitated as described above.

Radiocobalt containing complexes were counted by determining the activity of a standard volume of the solution of the complex when placed in a standard size test tube and inserted in the well of a scintillation counter. The isotope was  $Co^{60}$ , supplied by the Oak Ridge National Laboratory.

Experimental Procedures. (a) Aqueation Runs. A solution of the perchlorate salt of the complex being studied, usually 0.02M, was acidified with perchloric acid to a pH of ca. 2.5, and then thermostatted to within 0.1°C of the desired temperature. Small additional amounts of acid were added as needed to maintain the pH during the course of the run; it was found that pH control was not critical provided the pH was not allowed to rise beyond four or five. Aliquots were withdrawn and the free thiocyanate present determined spectrophotometrically. In some cases the samples when cooled to room temperature were supersaturated with respect to complex, in which case the complex was partially removed by perchlorate precipitation prior to the thiocyanate analysis.

Concentrations given for the various runs are accurate to 1%.

(b) Exchange Runs. The runs with  $C^{14}$  active complexes were carried out as above, except that the perchlorate salt of the complex was precipitated, washed with water, alcohol and ether, dried and counted, or cuprous thiocyanate samples were prepared from the free thiocyanate present, as described in the preceding section. For the runs at high complex concentration, the inactive thiocyanate salts of the active complex were employed, and thiocyanic rather than perchloric acid was employed to adjust the pH.

For the runs with  $Co^{60}(NH_3)_5(SCN)^{++}$ , it was necessary to count the resulting few percent of  $Co^{60}(NH_3)_5(H_2O)^{+++}$  formed. By means of a controlled precipitation, about 95% of the thiocyanato complex could be removed as the perchlorate salt, leaving about 95% of the aquo complex in the supernatant. Inactive thiocyanato complex was then added to this supernatant, the solution warmed slightly, and  $[Co(NH_3)(SCN)](ClO_4)_2$  again precipitated. By means of three such "washings" with inactive thiocyanato complex, about 85% of the active aquo complex remained and only ca. 0.1% of the original active thiocyanato complex.

### Experimental Results

Preliminary conventional exchange experiments, employing radiothiocyante ion and inactive trans  $\text{Co en}_2(\text{SCN})_2^+$  are shown in Figure 1. Not until  $80^\circ\text{C}$ . was there an appreciable rate of appearance of activity in the complex, and the McK. plots<sup>21</sup> shown in the figure failed to show linear behavior unless some two

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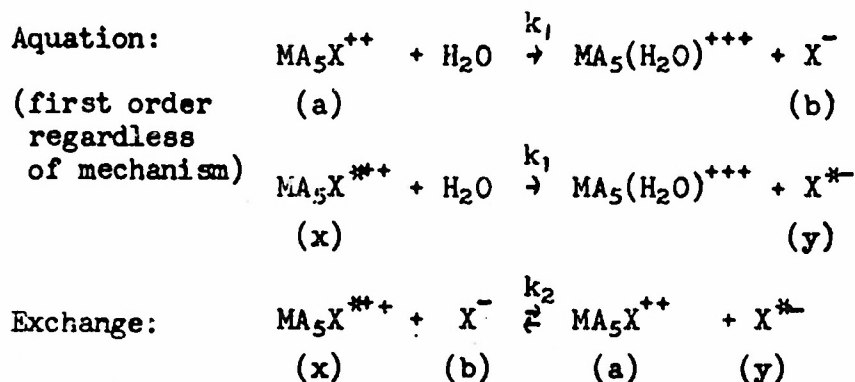
21 H. A. C. McKay, Nature, 142, 997 (1938)

days of pre-equilibration were allowed before adding the small amount of radiothiocyante to the solution of complex plus inactive thiocyante. In this figure,  $y$  and  $y^\infty$  denote the amounts of activity in the complex at time  $t$  and at exchange equilibrium. That this behavior resulted from a gradual attainment of aquation equilibrium was made probable by the results of separate aquation rate studies, shown in Figure 2. It is seen that the rates are commensurate with the pre equilibration times found necessary for the exchange runs. The data may be represented to within ca. ten percent by an equilibrium constant of 0.030 for the first stage of aquation, and a first order aquation constant of  $0.060 \text{ hr}^{-1}$ ; these are approximate because of the lack of ionic strength buffering, the presence of some extent of the second stage of aquation, and the probable trans to cis isomerization also occurring.

These and similar preliminary results with  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$  indicated that any bimolecular exchange would be comparable in rate to that through the aquation path, and that a means of detecting the former against a high background of the latter would be necessary. Conventional exchange studies with equilibrium systems were ruled out since the time required to reach aquation equilibrium also sufficed for some further decomposition of the complex. Exchange was therefore studied at temperatures such that the aquation was known

accurately, but for times short enough that only a few percent aquation would occur. If radiothiocyanate ion were used, and the rate of appearance of activity in the complex determined, then, ideally, a non-zero initial exchange rate would be attributable to a direct or bimolecular exchange. Experimentally, such a non-zero initial rate was found but was due to the fact that even upon repeated recrystallizations one or two percent of aquocomplex would remain as an impurity in the thiocyanato complex. Thus with 0.02 M  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$  and 0.0059M  $\text{SC}^{14}\text{N}^-$  at 70°C,  $d(S/S^0)/dt = k$  was  $0.019 \text{ hr}^{-1}$ , where  $S$  is the specific activity of the complex at time  $t$ , and  $S^0$  the value corresponding to the initial specific activity of the radiothiocyanate. On repeating the experiment with ten percent or 0.002M added aquo complex present initially,  $k$  rose to  $0.066 \text{ hr}^{-1}$  and the first results could therefor be due to the presence, on the average, of a few percent of aquo complex. That this was true was shown by the results described below, which set a much lower limit to the maximum rate of any direct exchange.

The procedure finally adapted involved the use of radioactive complex and the determination of the rate of increase of the specific activity of the free thiocyanate ion also present. The system of rate equations then becomes, for short times:



where  $x, y$  and  $a, b$  are the moles per liter of radiothiocyanate and of total thiocyanate in the two forms. Also  $x^0 = x + y$ ,  $c^0 = a^0 + b^0 = a + b$ , where the

superscript denotes the initial value, and  $S_x = x/a$ ,  $S_x^0 = x^0/a^0$ . The resulting rate equations are

$$dx/dt = -k_1x - k_2xb + k_2ay$$

$$dS_x/dt = -k(c^0S_x - a^0S_x^0)$$

and

$$S_x/S_x^0 = \frac{1}{c^0}[a^0 + b^0 \exp.(-c^0k_2t)]$$

which reduces to the McKay equation if  $k_1 = 0$ . If  $P$  is the increase in concentration of free thiocyanate that would correspond to the observed increase in  $S_y$  (i.e. assuming no exchange), then

$$P = S_y b^0 / (S_x^0 - S_y)$$

and if  $F$  be defined as the fraction of such apparent aquation,  $F = P/a^0$ , then

$$dF/dt = k_{app.} = k_1 + b^0k_2 \quad (\text{at short times}) \quad (2)$$

Thus any direct exchange should appear as a dependence of  $k_{app.}$  on the free thiocyanate concentration.

Aquation and Exchange of  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$ . The results are summarized in Figure 3 in which are plotted as a function of time both the apparent aquation in the presence of added thiocyanate and the true aquation as measured spectrophotometrically with no free thiocyanate initially present. Considering first the data at  $50^\circ\text{C}$ , it is seen that the radiochemically determined values of  $F$  for  $b^0 = 0$  agree well with the spectrophotometric ones, confirming the accuracy of the two techniques. However, for  $b^0 = 0.02\text{M}$  at  $50^\circ$ , and  $0.2\text{M}$  at  $70^\circ$ , no change in  $k_{app.}$  was detectable. Thus  $b^0k_2$  was less than a few percent of  $k_1$ ; at  $70^\circ\text{C}$ ,  $k_2$  in  $\text{hr}^{-1}\text{M}^{-1}$  was less than 0.015.

Aquation and Exchange of  $\text{Co}(\text{NH}_3)_4(\text{SCN})$ . These results are given in Figures 4 and 5. It is seen that at  $90^\circ\text{C}$ , the apparent aquation rate increased several fold in the presence of up to  $0.5\text{M}$  added thiocyanate ion. Although concordant

values of  $k_2$  result from the application of equation (2) to the data, the possibility remained that the aquation rate itself, i.e.  $k_1$ , was varying. Thus Garrick<sup>9c</sup> found that the aquation rate of  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  varied with the nature of the anion, and Taube and Posey<sup>9e</sup> likewise for  $\text{Co}(\text{NH}_3)_5(\text{SCN})^+$ . Since such an effect, if any, occurred in the present work only at high free thiocyanato to complex ratios, the spectrophotometric method was insufficiently accurate. The procedure finally adapted was that of employing  $\text{Co}^{60}$  labelled  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$  and determining the rate of production of radioactive aquo complex, as described under Experimental. Because of the elaborate procedure, the results suffered in precision, but, as shown in Figure 5, clearly demonstrated that the aquation rate increased with free thiocyanate concentration to the same degree as did the apparent aquation rates previously determined. This anion effect on the aquation rate may be represented by the equation  $k_1(\text{hr}^{-1}) = 0.019 + 0.029(\text{SCN}^-)$ , at  $90^\circ\text{C}$ .

Aquation and Exchange of trans.  $\text{Coen}_2(\text{SCN})_2^+$ . The results are given in Figure 6. This system was studied in less detail because of the curvature in the rate plots even at short times, presumably due to a trans to cis isomerization. Again, however, the apparent aquation rate with  $b^0 = 0.05\text{M}$  was the same as the spectrophotometric value, although an increase was found in the presence of  $0.5\text{M}$  chloride ion.

Summary of Aquation Data. The temperature dependence of the aquation rate constants for  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$  and  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$  is shown in Figure 7, and data are summarized in Table I, with results for other pentamine complexes included for purposes of comparison.



Table I  
Aquation of Acidopentamine Complexes at 25°C.<sup>a</sup>

Complex	$k_{\text{min}}^b$	$\Delta H^d$	$\Delta S^c$
$\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$	$1.7 \times 10^{-7}$	26.8	-8.4
(Cl)	$1.2 \times 10^{-4}$	23.7	-1.3
(NO <sub>3</sub> )	$1.6 \times 10^{-4}$	26.0	7.1
(Br)	$3.8 \times 10^{-4}$	24.0	-2.4
$\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$	$5.6 \times 10^{-6}$	24.9	-7.8
(Cl)	$4.8 \times 10^{-4}$	21.8	-8.8
(Br)	$3 \times 10^{-3}$	22	-5
(I)	$10^{-2}(0^\circ\text{C})$		

(a) Values for other than the thiocyanato complexes from J. N. Bronsted and R. Livingston, THIS JOURNAL, 49, 435 (1927).

(b) Calculated values.

(c) Calculated on the basis of a frequency factor of  $10^{13} \text{ sec}^{-1}$ .



It is seen that for the pentamine complexes the order of increasing aquation rate is SCN, Cl, Br, I, and that the cobalt(III) complexes aquate more slowly than do the corresponding Cr(III) ones. These effects stem primarily from activation energy differences. Interestingly, while thiocyanate ion catalysed the aquation of  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$ , it did not catalyse that of  $\text{Cr}(\text{NH}_3)_5(\text{SCN})^{++}$ , yet in the studies of water exchange, the exchange of  $\text{H}_2\text{O}^{18}$  with  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$  was first order in anion<sup>12</sup> while the exchange with  $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{+++}$  was unaffected or slightly retarded by sulfate ion.<sup>13</sup>

Ion Pair Formation. In view of the anion effects found here, the absorption spectra of the various complexes were determined with and without the presence of added thiocyanate ion. Evans and Nancollas<sup>21</sup>

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21 M. G. Evans and G. H. Nancollas, Trans. Far. Soc., 49, 363 (1953).

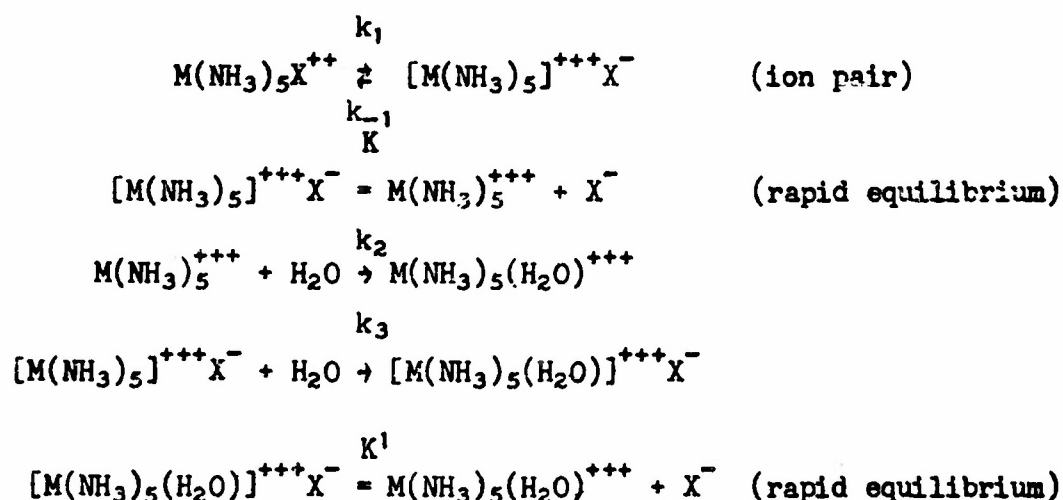
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found that with  $\text{Co}(\text{NH}_3)_6^{+++}$  ion pair formation occurred with halide and with azide ions, with considerable shifts in the extinction coefficient of the complex in the wave length region 200-300 mμ. Although as complete a study was not made here, it is apparent from Figure 8 that the spectra of  $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{+++}$  and  $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{+++}$  are drastically shifted in this wave length region. Those of the thiocyanato complexes were unaffected. Presumably, the ion pair formation is extensive between  $\text{SCN}^-$  and  $\text{M}(\text{NH}_3)_5\text{H}_2\text{O}^{+++}$ , but not between  $\text{SCN}^-$  and  $\text{M}(\text{NH}_3)_5(\text{SCN})^{++}$ .

## Discussion

The present results and those cited in the introduction have indicated that with hexacoordinated complex ions the bimolecular or  $S_N2$  replacement of ligands does not occur except insofar as it contributes to the aquation process. There remains the question of whether the specific anion effects observed in the aquation and water exchange reactions with positively charged complex ions permit reasonable inferences.

In view of the results of Evans and Nancollas<sup>22</sup> as well as those of Olson and Simonson<sup>9</sup> it seems reasonable to treat the specific anion effects as arising from ion pair formation, modifying either the reactants, or, in the case of an  $S_N1$  mechanism, the pentacoordinated intermediate as well. Considering this last possibility first, the mechanism given in the introduction could then be particularized as follows:



Assuming a stationary state restriction on the sum of the species  $M(NH_3)_5^{+++}$  and  $[M(NH_3)_5]^{+++}X^-$ , the rate law becomes:

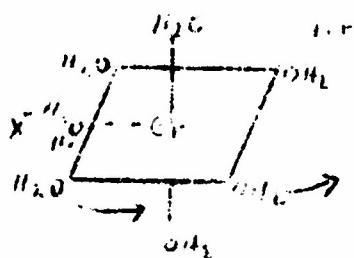
$$R = \frac{k_1 [M(NH_3)_5X^{+++}]}{1 + k_{-1}/[k_3 + k_2K/(X^-)]}$$

However, as  $(X^-)$  increases,  $R$  decreases from the upper limit  $k_1[M(NH_3)_5X^{++}]$  to the lower limit  $\frac{k_1[M(NH_3)_5X^{++}]}{1 + k_{-1}/k_3}$ , which is the opposite of the observed effect.

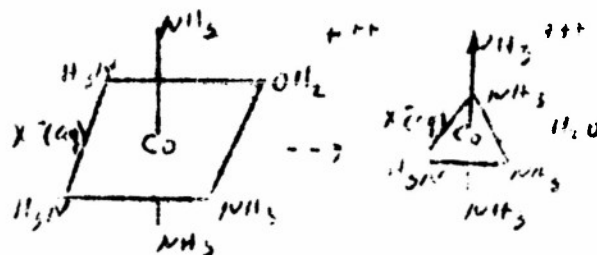
It thus appears that the specific anion effects must result from ion pair formation with the reactant species, regardless of mechanism. Therefore, the fact that essentially opposite effects are found for the chromium and the cobalt complexes, both in the case of aquation and in that of water exchange, strongly suggests that different mechanisms are important in the two cases. It might be supposed that the  $S_N1$  mechanism should be about equally available to both chromium and cobalt complexes, but that the chromium ones should, in addition, have a lower energy path for reaction through the  $S_N2$  process. This would explain qualitatively the greater lability of the chromium complexes, as evidenced by their aquation rates, and would be in agreement with the observation of Brown et al<sup>10</sup> that the second order ligand replacements in  $Coen_2Cl_2$  in methanol were faster than those proceeding by first order kinetics, if one accepts their conclusion that the former represented an  $S_N2$  and the latter an  $S_N1$  process.

A reasonably consistent explanation of the various anion effects can be made with this assumption that the trivalent chromium complexes do react primarily through the  $S_N2$  mechanism and those of cobalt through the  $S_N1$  mechanism. Accepting the edge displacement hypothesis of Brown et al, as applying to  $S_N2$  processes, then the exchange of water with  $Cr(H_2O)_6^{+++}$  involves the displacement of identical groups. The strong ion pairing that would be present might favor the displacement process through orienting effect of the anion on the outer sphere waters as was suggested by Taube et al<sup>12</sup>. For  $Cr(NH_3)_5X^{++}$ , not only would ion pairing be much weaker, but since the ion paired anion would tend to be on a side away from the bound

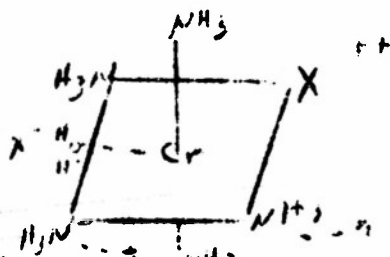
anion, it could not influence edge displacement leading to aquation. For the cobalt complexes, assuming an  $S_N1$  mechanism, the transition state leads to a pentacoordinated intermediate, and the edge displacement picture does not apply. Since the rate determining step here appears to be the formation of the intermediate, the rate of substitution processes would be affected by ion pairing in the reactant only through general attraction or repulsion effects. Thus, for the water exchange with  $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})^{++}$ , although strong ion pairing would occur, no particular effect on the rate of dissociation of a neutral water molecule would be expected, nor is observed. Rutenberg and Taube<sup>13</sup> commented that the slight retardation in this exchange, in the presence of sulfate ion, constituted strong evidence for an  $S_N1$  mechanism. On the other hand, the aquation of  $\text{Co}(\text{NH}_3)_5\text{X}^{++}$  might well be anion influenced since some ion pairing would be expected even with a divalent ion, and the charge repulsion between the inner and outer X groups should favor the dissociation of the inner group. The above representations are illustrated below.



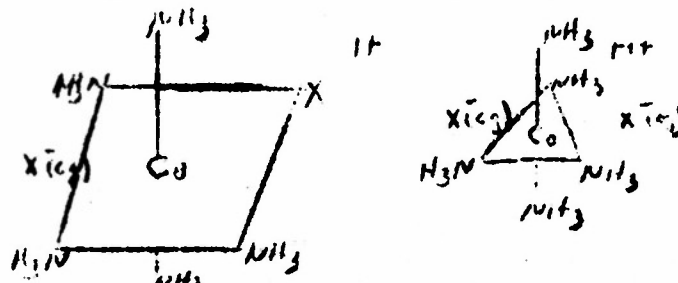
$\text{H}_2\text{O}$  exchange catalyzed by  $\text{X}^-$



$\text{H}_2\text{O}$  exchange not catalyzed by  $\text{X}^-$



Aquation not catalyzed by  $\text{X}^-$



Aquation catalyzed by  $\text{X}^-$

(The actual geometry of the pentacoordinated intermediate is not known,

and the one chosen is for illustrative purposes.)

Brown et al<sup>10</sup> consider that the second order kinetics of the hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  9a,b and of the substitution in methanol solution of  $\text{Cl}^-$  in  $\text{Coen}_2\text{Cl}_2^+$  by nucleophilic ions such as methoxide<sup>10</sup> to be evidence for an  $\text{S}_\text{N}2$  mechanism in these cases. While this may be correct, it is noteworthy that the preceding discussion of ion pair effects accounts for anion dependencies in some cases strong enough to give rates first order in anion or second order overall. Thus the  $\text{SCN}^-$  effect on the aquation rate of  $\text{Co}(\text{NH}_3)_5(\text{SCN})^{++}$  was expressible by the rate law  $k_1 = 0.019 + 0.029(\text{SCN})^-$ . Had the anion effect been somewhat stronger, a simple second order rate expression would have been found. It is thus possible that the second order kinetics of hydrolysis is in this category, with the anion adding to a penta-coordinated  $\text{S}_\text{N}1$  intermediate as well as catalyzing its formation. Although Brown et al dealt with 1-1 electrolytes, in methanol solution some ion pairing would still be expected, and ionic strength effects were in fact noted in the first order rate constants computed for the displacement by halide and thiocyanate ions. In order to evaluate the possibility that the second order displacement kinetics observed with methoxide, azide and nitrite ions might correspond to a higher degree of ion pair catalysis, rather than to a change in mechanism, studies on ion pair formation in this solvent would be necessary.

LOS ANGELES, CALIFORNIA

## Legends for the Figures

- Figure 1 "Equilibrium" Exchange between  $\text{SC}^*\text{N}^-$  and  $0.038\text{M Trans [Coen}_2(\text{SCN})_2]^+$  at  $80^\circ\text{C}$ ., pH 6.5  
 $\diamond$ ,  $\Delta(\text{SC}^*\text{N}^-) = 0.277\text{M}$ , 2 hrs. pre-equilibration;  $\square$ , 2 days pre-equilibration;  $\circ$ , 4 days pre-equilibration;  $\bigcirc$  ( $\text{SC}^*\text{N}^-$ ) =  $0.157\text{M}$ , 4 days pre-equilibration.
- Figure 2 Aquation of  $\text{Trans[Coen}_2(\text{SCN})_2]^+$ ,  $\text{A}$ , at  $80^\circ\text{C}$ ., pH 6.5  
 $\circ$ ,  $\text{A} = (\text{ClO}_4^-) = .0125\text{M}$ ;  $\Delta$ ,  $\text{A} = (\text{SCN}^-) = 0.01\text{M}$ ;  $\square$ ,  $\text{A} = (\text{SCN}^-) = .0500\text{M}$ .
- Figure 3 Aquation and Exchange of  $[\text{Cr}(\text{NH}_3)_5(\text{SC}^*\text{N})](\text{ClO}_4^-)_2$ ,  $\text{A}^*$ , at pH 2.5  
 $80^\circ\text{C}$ .,  $\circ$ ,  $\text{A} = 0.01\text{M}$ ;  $70^\circ\text{C}$ .,  $\circ$ ,  $\text{A} = 0.02\text{M}$ ,  $\square$ ,  $\text{A} = 0.02\text{M}$  and  $(\text{SCN}^-) = 0.055\text{M}$ ,  $\bullet$ ,  $\text{A} = 0.2\text{M}$  and  $(\text{SCN}^-) = 0.4\text{M}$  (no  $\text{ClO}_4^-$ );  $60^\circ\text{C}$ .,  $\circ$ ,  $\text{A} = 0.01\text{M}$ ;  $50^\circ\text{C}$ .,  $\circ$ ,  $\text{A} = 0.01\text{M}$ ,  $\bullet$ ,  $\text{A} = 0.01\text{M}$ ,  $\square$ ,  $\text{A} = 0.01\text{M}$ ,  $(\text{SCN}^-) = 0.02\text{M}$ .
- Figure 4 Aquation and Exchange of  $[\text{Co}(\text{NH}_3)_5(\text{SC}^*\text{N})](\text{ClO}_4^-)_2$ ,  $\text{A}^*$ , at  $90^\circ\text{C}$ , pH 2.5  
 Spectrophotometric:  $\circ$ ,  $\bullet$ ,  $\text{A} = 0.02\text{M}$ ;  $\text{C}^{14}$  labelled complex:  $\bullet$ ,  $\text{A}^* = 0.02\text{M}$ ,  $\Delta$ ,  $\text{A} = 0.07\text{M}$  and  $(\text{SCN}^-) = 0.54\text{M}$  (no  $\text{ClO}_4^-$ );  $\circ$ ,  $\text{A} = 0.167\text{M}$  and  $(\text{SCN}^-) = 0.33\text{M}$  (no  $\text{ClO}_4^-$ );  $\text{Co}^{60}$  labelled complex:  $\square$ ,  $\text{A} = 0.07\text{M}$  and  $(\text{SCN}^-) = 0.55\text{M}$  (no  $\text{ClO}_4^-$ ),  $\Delta$ ,  $\text{A} = 0.02\text{M}$ .
- Figure 5 Aquation Rates for  $[\text{Co}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4^-)_2$ . (Complex) =  $0.02\text{M}$ , pH = 2.5
- Figure 6 Aquation and Exchange of  $\text{Trans[Coen}_2(\text{SC}^*\text{N})_2](\text{ClO}_4^-)_2$ ,  $\text{A}^*$ , at  $80^\circ\text{C}$ ., pH 6.5.  
 $\circ$ ,  $\text{A} = 0.05\text{M}$ ;  $\bullet$ ,  $\text{A}^* = 0.05\text{M}$ ;  $\square$ ,  $\text{A}^* = 0.05\text{M}$ ,  $(\text{SCN}^-) = 0.05\text{M}$ ;  $\text{A} = 0.05\text{M}$ ,  $\text{Cl}^- = 0.05\text{M}$
- Figure 7 Temperature Dependence of the Aquation Rates  
 $\circ$ ,  $[(\text{Cr}(\text{NH}_3)_5(\text{SCN}))](\text{ClO}_4^-)_2$ ;  $\Delta$ ,  $[\text{Co}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4^-)_2$  ( $k$  in  $\text{min}^{-1}$ )
- Figure 8 Absorption Spectra  
 AA,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4^-)_3$ ; B, same as AA but with  $0.3\text{M}$  added  $\text{SCN}^-$ ;  
 CC,  $[\text{Co}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4^-)_2$  (no effect with added  $\text{SCN}^-$ );  
 DD,  $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4^-)_3$ ; F, same as DD, but with  $0.3\text{M}$  added  $\text{SCN}^-$ ;  
 EE,  $[\text{Cr}(\text{NH}_3)_5(\text{SCN})](\text{ClO}_4^-)_2$  (no effect with added  $\text{SCN}^-$ ).

